Structure-Property Relations in Transuranic Compounds

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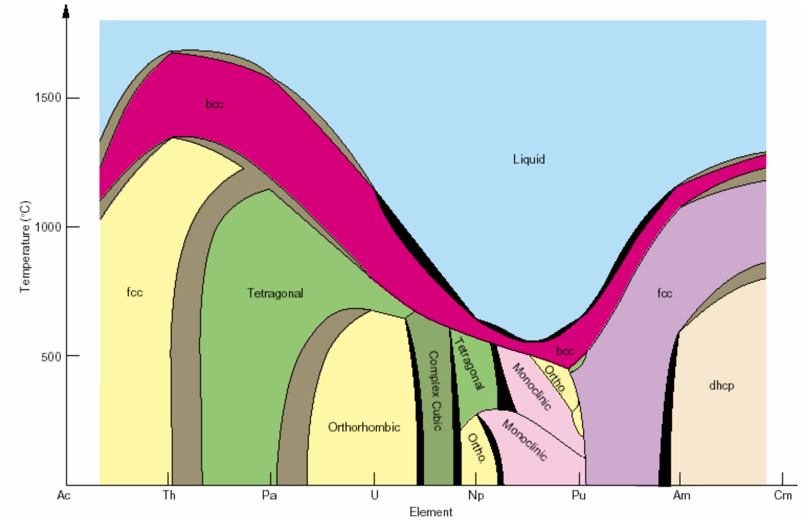
Objective: Advance the fundamental understanding of structure and bonding in transuranic intermetallics and molecular systems

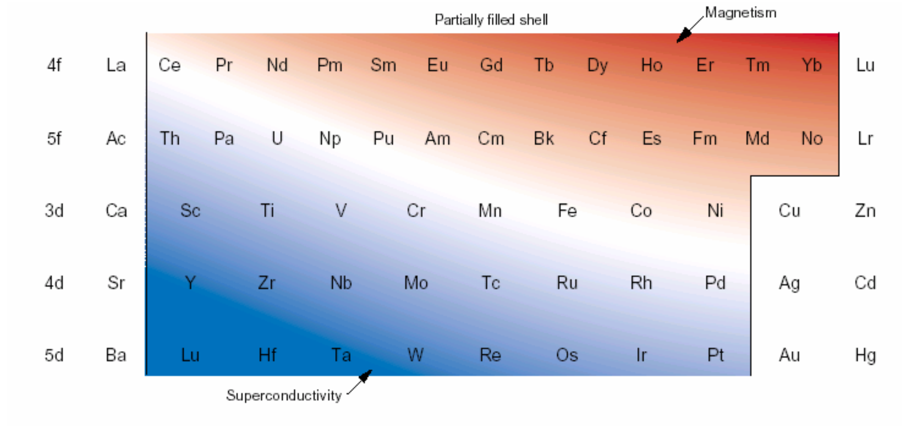
Office of Basic Energy Sciences • Serving the Present, Shaping the Future •

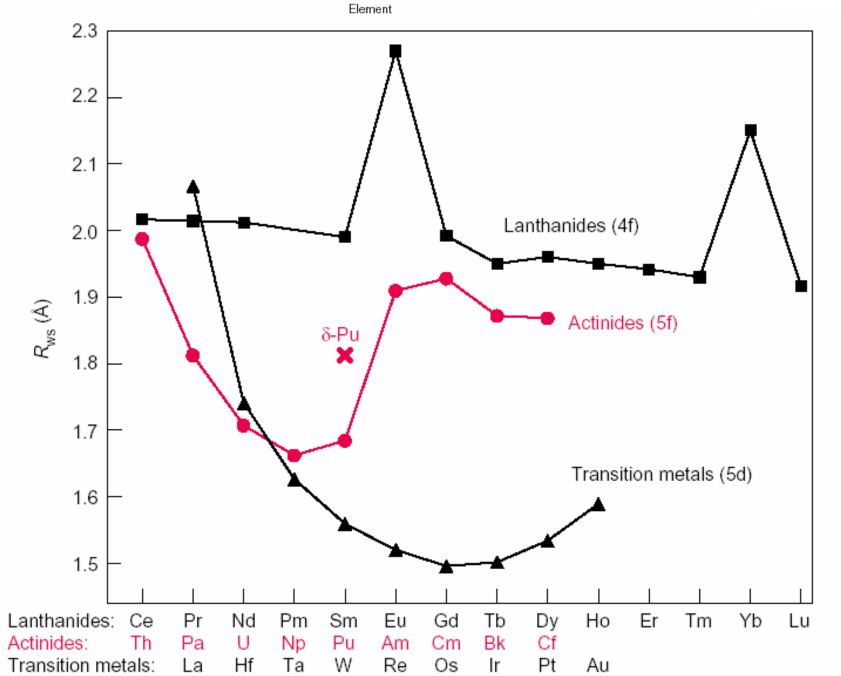
CSP Proposal, June, 2004

Office of Science
U.S. DEPARTMENT OF ENERGY

An important problem: Strong tunability in actinides influences properties







- Localized-itinerant transition in 5f electrons drives behavior
- Manifestations in spin, charge, and lattice degrees of freedom
- Technological consequences

A renaissance -- in high-visibility results

Reaction of plutonium dioxide with water: Formation and properties of PuO_{2+x}
SCIENCE 287 (2000) 285-287

Correlated electrons in delta-plutonium within a dynamical mean-field picture
NATURE 410 (2001) 793-795

Plutonium-based superconductivity with a transition temperature above 18 K
NATURE 420 (2002) 297-299

Calculated phonon spectra of plutonium at high temperatures
SCIENCE 300 (2003) 953-955

First-principles calculations of $PuO_{2\ +/-\ x}$
SCIENCE 301 (2003) 498-501

Phonon dispersions of fcc delta-plutonium-gallium by inelastic X-ray scattering
SCIENCE 301 (2003) 1078-1080

Failure of Russell-Saunders coupling in the 5f states of plutonium
PHYSICAL REVIEW LETTERS 90 (2003) 196404

Photoemission and the electronic structure of $PuCoGa_5$
PHYSICAL REVIEW LETTERS 91 (2003) 176401

A renaissance -- in outreach, coordination

MRS Symposium DD: Actinides—Basic Science, Applications, and Technology

(Fall, 2003: Tobin (LLNL), Joyce (LANL), Soderholm (ANL) et al.)

(Fall, 2005: Schwarz (LLNL), Sarrao (LANL))

Actinide Science for the 21st Century:

A U.S. Department of Energy Chemical Sciences Council and National Science Foundation Workshop

(May, 2004; Shuh (LBNL), Clark (LANL))

Why a distributed center?

Specialized facilities demand it, but also:

bridging disciplines (chemistry – physics)

need for re-vitalization of community

opportunity for critical perspectives

International precedent:

The Actinide Association

Institute for Transuranic Elements, Karlsruhe

JAERI, Tokai

CEA, Grenoble

Why Us?

- Who we are
- Where we’re going
- What we learned at our workshop
- How we’ll spend your money

Core Team – Lab principals

John Sarrao (LANL, synthesis and characterization)
Corwin Booth (LBNL, spectroscopy)
Pat Allen (LLNL, spectroscopy)
Lynne Soderholm (ANL, synthesis and characterization)
& many others from LANL, LBNL, LLNL, ANL

Centers of activity

Illinois: ANL, APS
New Mexico: LANL
California: LBNL/SSRL/LLNL

Core Team – University Partners

Thomas Albrecht-Schmitt (Auburn; bulk synthesis)
Dick Andersen (UC Berkeley; molecular synthesis)
Peter Burns (Notre Dame; crystallography)
Daniel Cox (UC Davis; theory)
Zachary Fisk (UC Davis; NAS; bulk synthesis)
James Ibers (Northwestern; NAS; bulk synthesis)

- Demonstrated technical leadership

  in synthesis, characterization and spectroscopy

- Access to facilities
- Community building

  Geographical affinities AND technical affinities

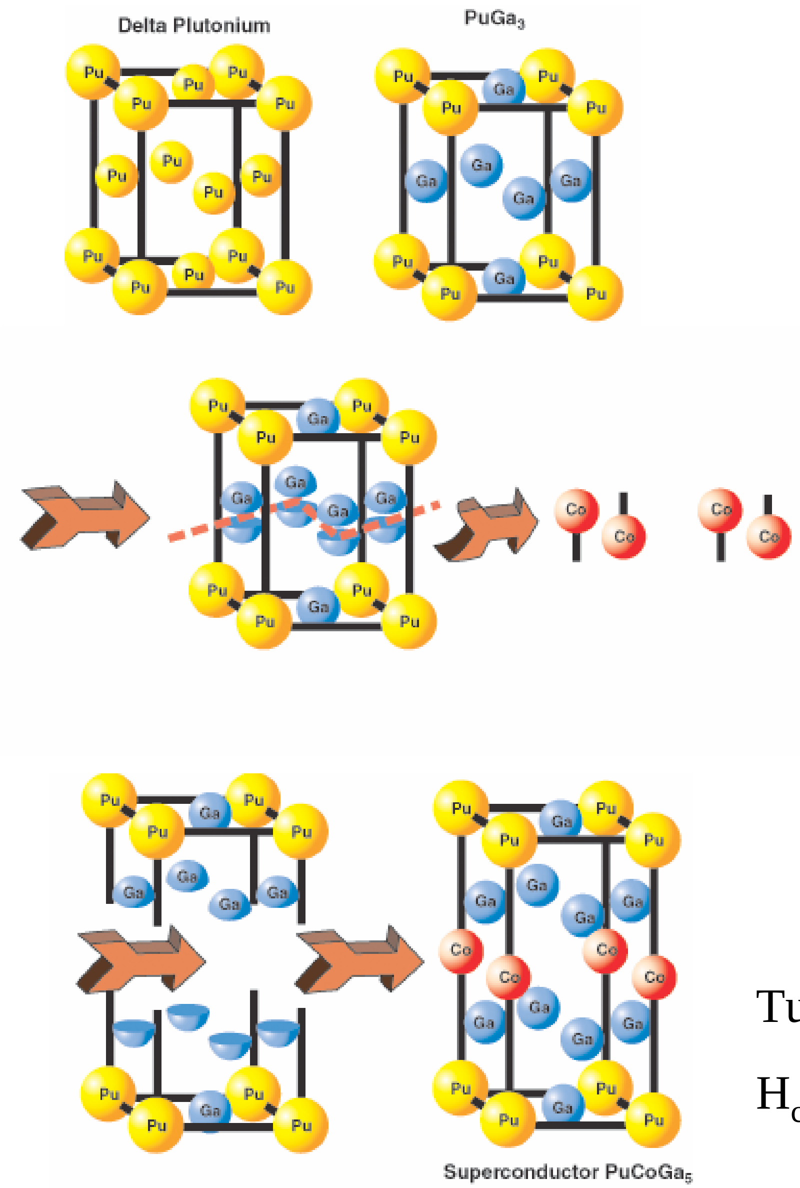
Integrating Themes

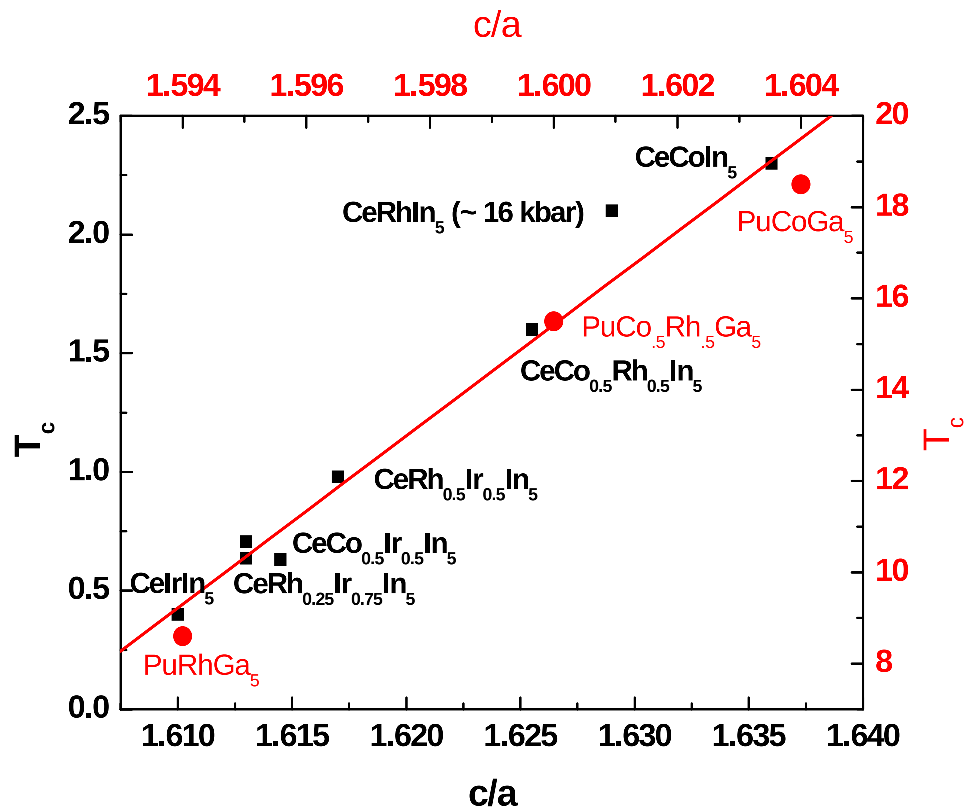
Design, discovery, and development of new material systems that are poised on the brink between localized and itinerant behavior

“Structure – Property Relationships”
    Understanding and Exploiting

Synergies among
    Synthesis – Characterization – Spectroscopy

Plutonium Superconductivity: $PuCoGa_5$





Tuning structural anisotropy enhances T_c.

H_{c2} ~ 100 T → High critical current → magnet applications

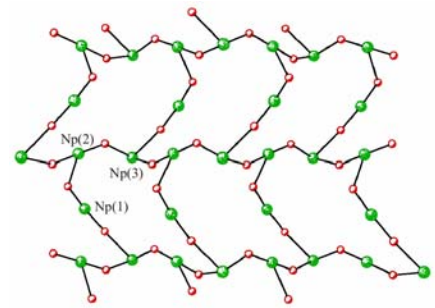
(at least in principle)

Structure-Property Relationships in Neptunium Selenites

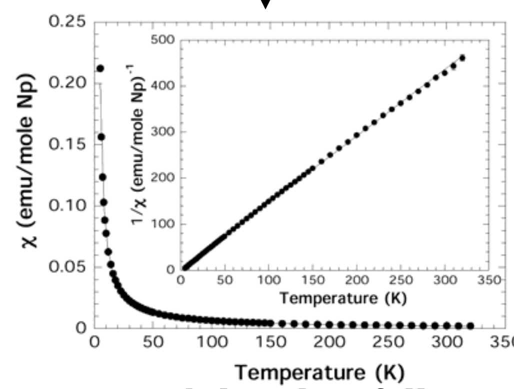
Hydrothermal Synthesis and Single Crystal Growth

$$NpO_2 + SeO_2 \xrightarrow[\text{CsCl, } H_2O\text{, 3d}]{180\ ^{o}C} \mathbf{Np(NpO_2)_2(SeO_3)_3}$$

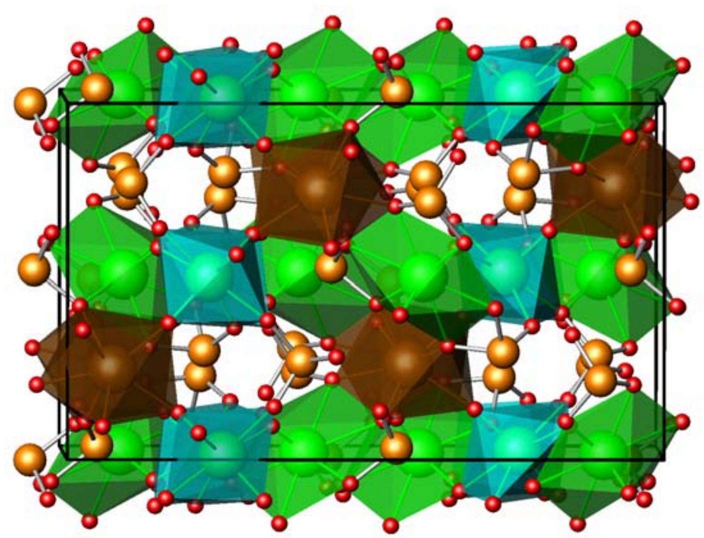
Hydrothermal conditions provide a facile and high-yield route to a variety of Np selenites.



Cation-cation interactions exist in the structure creating a 2D substructure



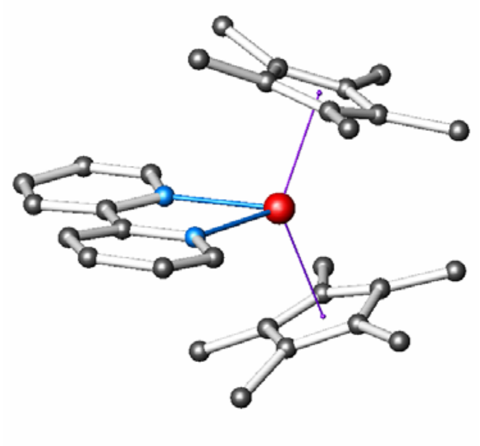
Magnetic susceptibility data follow Curie-Weiss behavior with a $\mu_{eff} = 2.28\ \mu_B$.



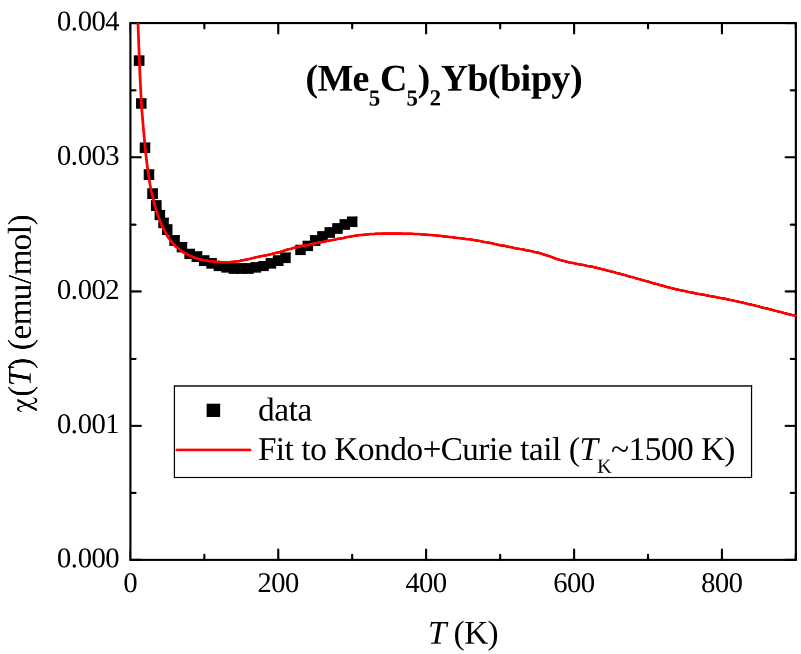
Crystal structure demonstrates that the compound contains both Np(IV) and Np(V) in different coordination environments.

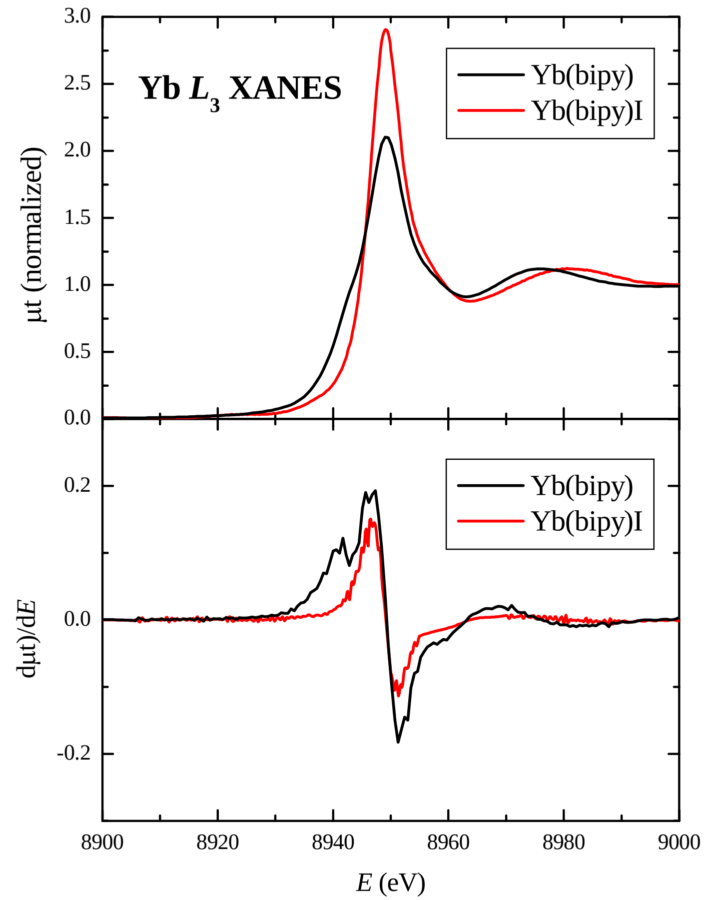
Future work will address Np selenites and iodates that may undergo magnetic ordering at low-temperatures. We will make use of single crystal magnetic susceptibility measurements, neutron diffraction, and X-ray absorption spectroscopy to better understand the electronic coupling.

Adducts of $(Me_5C_5)_2Yb$ Related to 2,2'Bipyridine

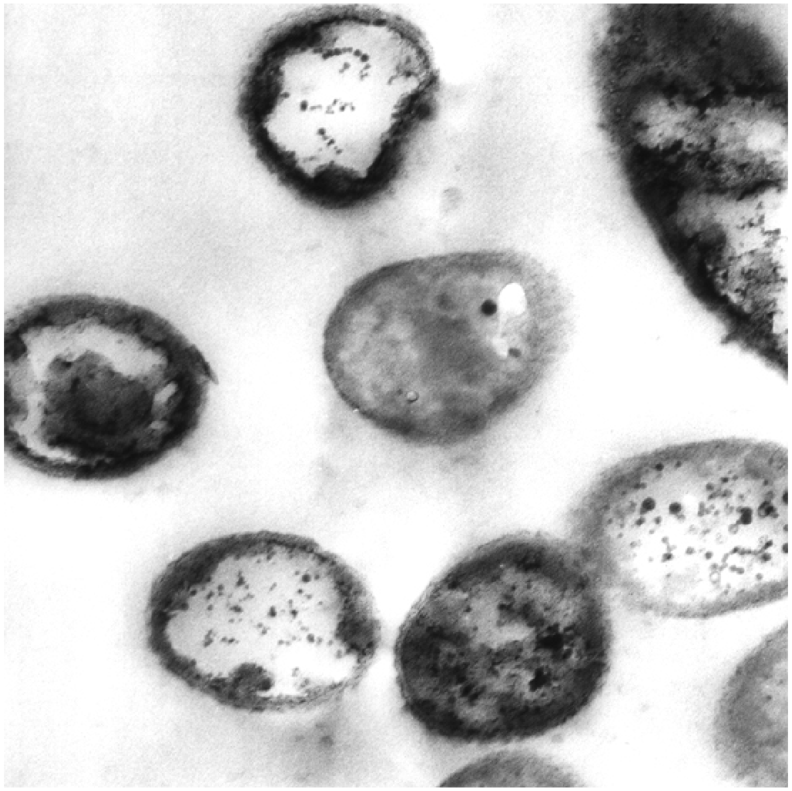


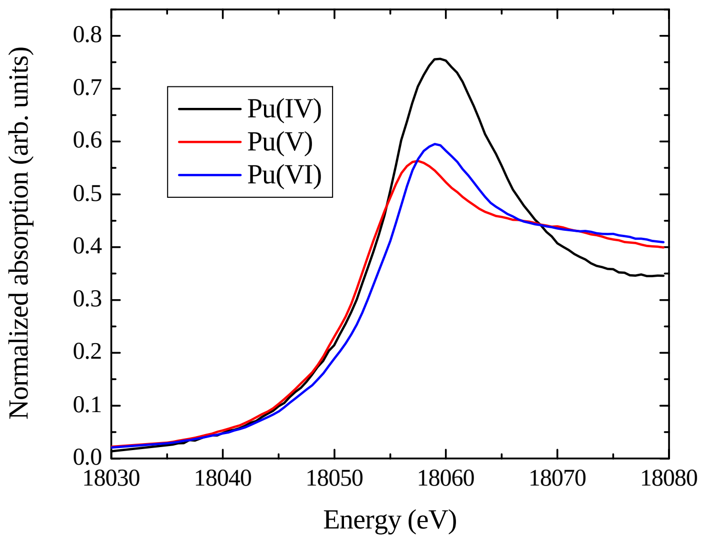
Cp^*_2 Yb (bipy)
Cp^*_2 Yb (p-methyl-dad)

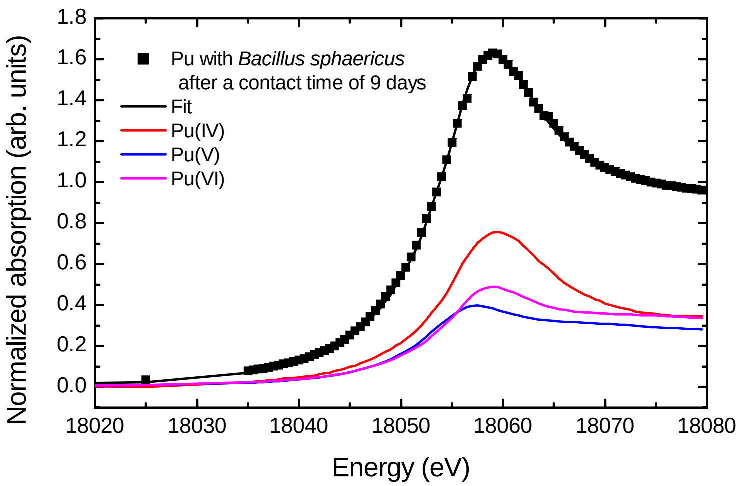




Actinides in bacteria – implications for remediation







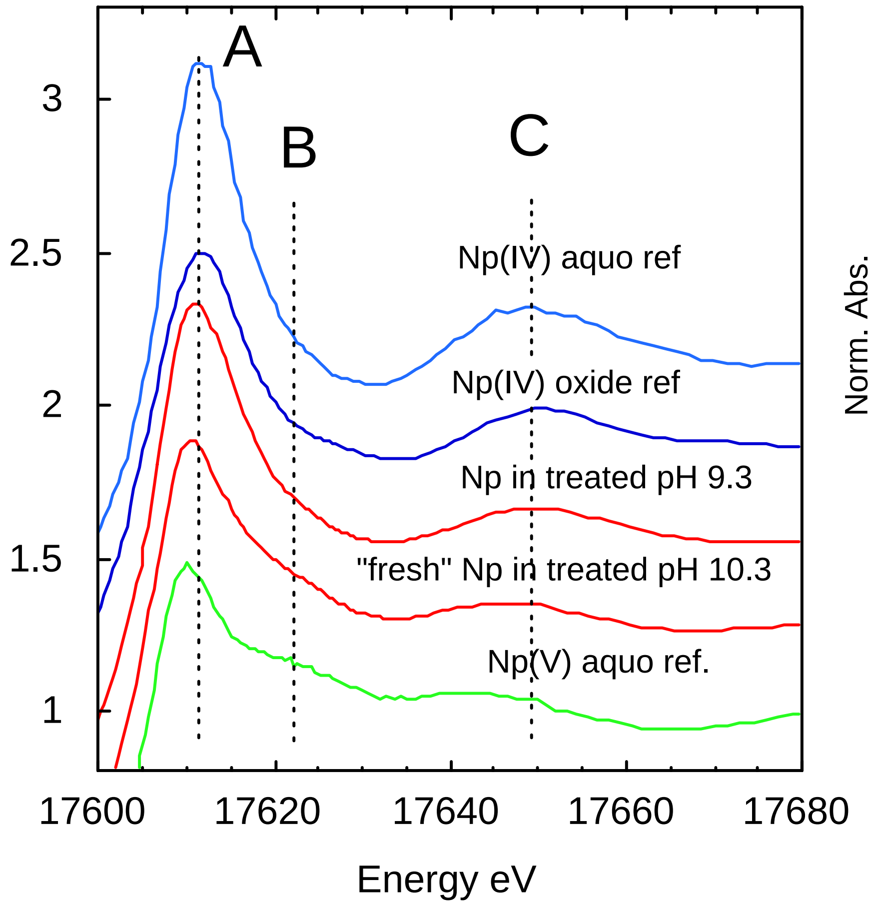
- possibility exists for certain bacteria to express phosphate
- These phosphates may complex with UO_2^{2+} under aerobic conditions.
- “Converting” UO_2^{2+} into a phosphate is beneficial because U-phosphates are less soluble than uranyl.
- A procedure exists to remove such actinides from a solution…

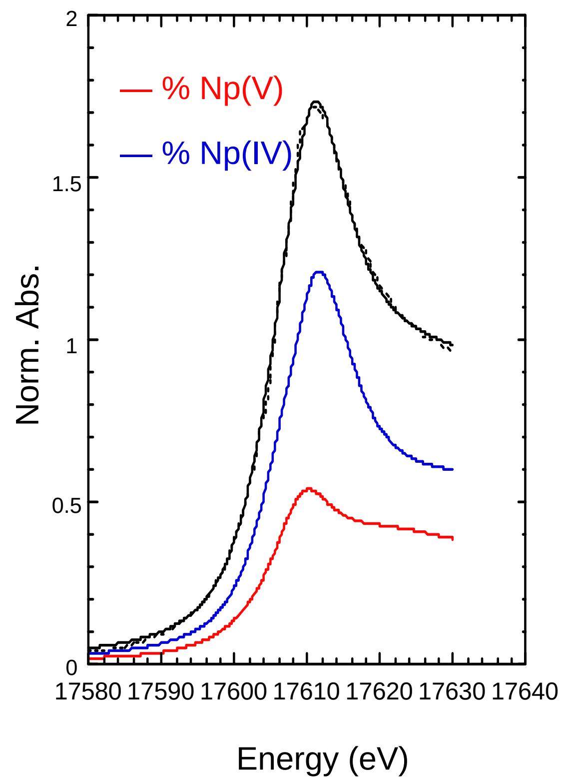
Np(V) Interaction with Cementitious Materials

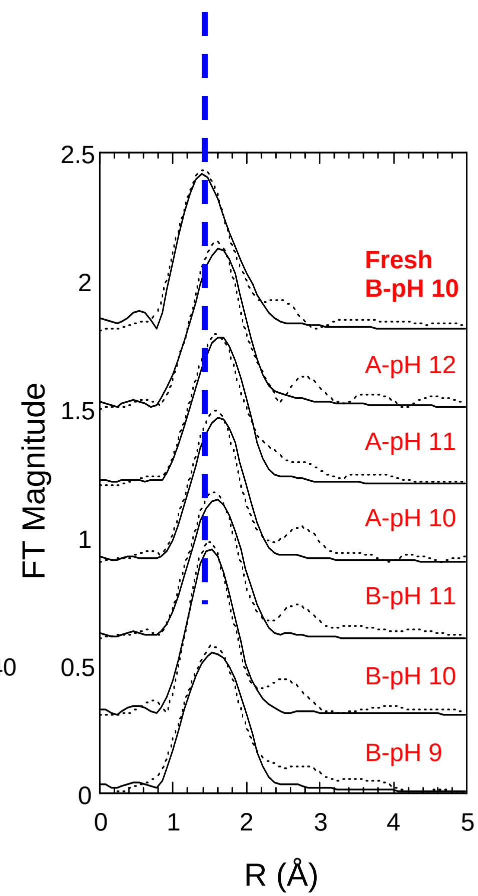
XANES indicates
$NpO_2^+ \rightarrow Np^{4+}$

PCA analysis

EXAFS shows
Avg. lengthening of Np—O Bonds



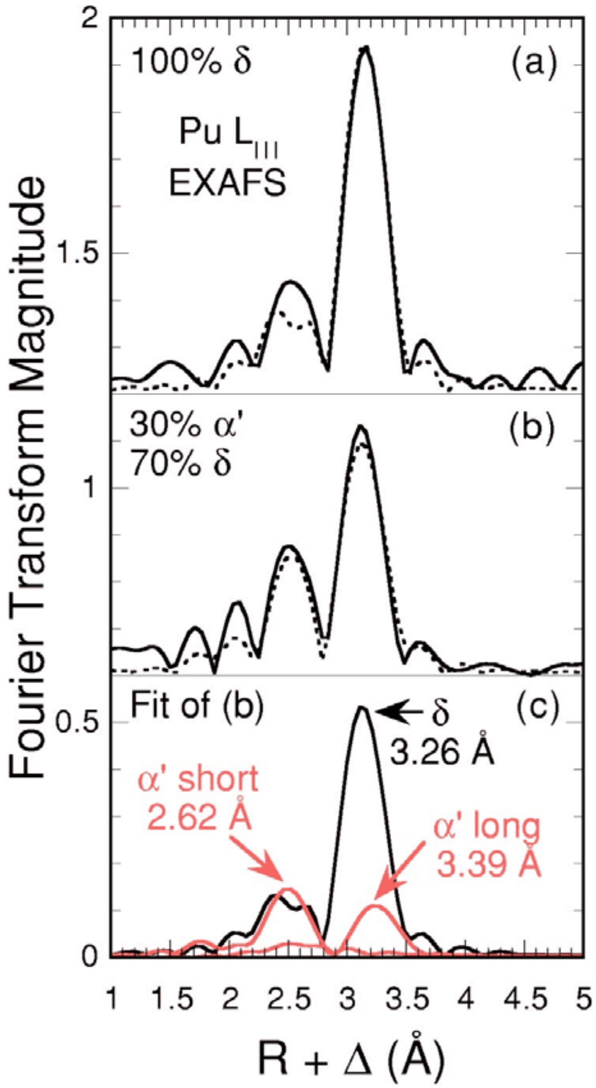




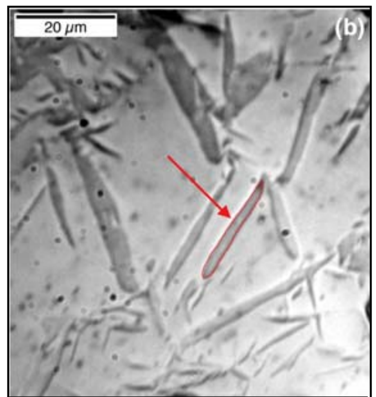
XANES and EXAFS indicate reduction Np(V) —> Np(IV)

Phase specific vibrational data from EXAFS

Pu EXAFS



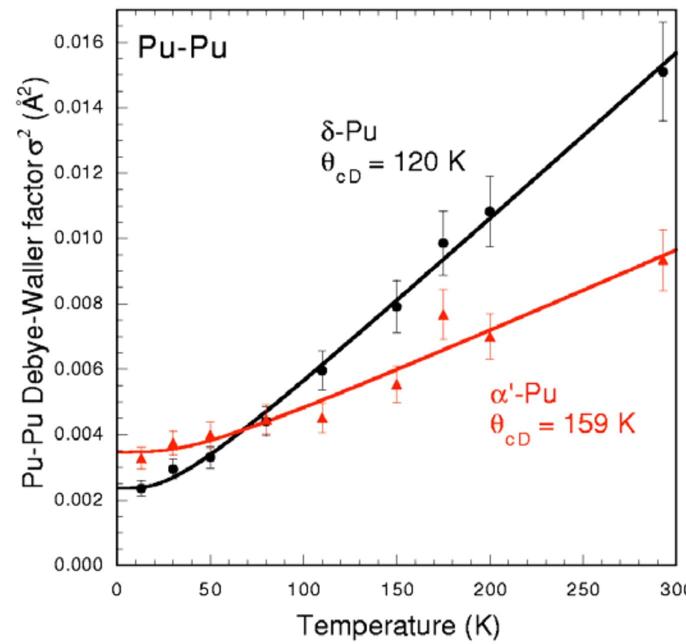
mixed phase
“martensite”



30% α’ 70% δ
1.9 at% Ga

Ga in α-Pu Bonds is also separable!

α'-Pu and δ-Pu
Pu—Pu Displacements
Fitted to "Debye" Model



Similar opportunities with valence spectroscopies

What we’ve learned

(including your feedback from December)

Localization and itinerancy (Bonds vs Bands) a central issue

for science AND applications

Environmental tuning

Coordinated teaming essential (jargon/vocabulary a barrier)

Better engagement of BES-Chem Sciences community

Utility of advanced spectroscopies (e.g., NMR)

Science Focus

Bringing localization to bulk systems and itinerancy to molecules

Correlated solids

- Neptunium intermetallics at ANL
- Plutonium flux growth at LBNL w/ Fisk

Correlated molecules

- Extend Yb monomers to multimers and actinides
- Coupled chemical synthesis and physical measurements

Valence spectroscopy

- XANES and EXAFS, e.g., $PuCoGa_5$ at SSRL this week

Management Plan

Essential collaboration/communication among core team

~ Quarterly Principals Meetings

Post-docs and students as “glue”

between Labs

between Labs and Universities

-unique facilities are an asset here

Extended on-site workshops/ “schools”

Specific, annual themes ‘kicked off’ – e.g., actinide oxides

Broader impacts and opportunities

Same underlying physics as in many correlated electron systems (e.g., transition metal oxides)

A starting point for BES crystal growth centers

Building the next generation of actinide scientists

Strong coupling to Seaborg Institutes

Actinides in the environment

Partnering with Notre Dame EMSI (NSF); DOE-BER